Formation of poly(butylene terephthalate): Secondary reactions studied by model molecules

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The secondary reactions occurring in the formation of poly(butylene terephthalate), leading to thermal degradation (in the temperature range 210°–280°C) or giving rise to tetrahydrofuran (in the temperature range 160°–190°C) have been kinetically studied with the aid of model molecules: 1,4-butylene dibenzoate and 4-hydroxybutyl benzoate. Some kinetic parameters have been determined; the effect of temperature and of catalysts and stabilizers has been considered and a mechanism is proposed for the formation of tetrahydrofuran from hydroxyl end groups.

INTRODUCTION

In a previous paper[1] we have considered the whole of the desired and undesired reactions which can be reasonably assumed to take place during the formation of poly(butylene terephthalate) (PBT). In that paper we have shown how the use of suitable model molecules allowed us to study the 'useful' reactions, that is, the reactions by which the polymerization process is accomplished. It may be recalled here that 4-hydroxybutyl benzoate (HBB) was chosen as 'monomer' and 1,4-butylene dibenzoate (BDB) as 'polymer'.

This paper aims to complete the research by taking into account the undesired reactions, leading to polymers of poorer quality and to lower yields. Such reactions can be classified as follows:

(i) reactions leading to polymer degradation with decrease of molecular weight. In the model system these are represented by the following equations:

$$C_6H_5COO(CH_2)_4OCOC_6H_5 \rightarrow C_6H_5COOH + CH_2=CH(CH_2)_2OCOC_6H_5 \quad (A)$$

$$C_6H_5COO(CH_2)_2CH=CH_2 \rightarrow C_6H_5COOH + CH_2=CH-CH=CH_2 \quad (B)$$

(ii) reactions leading to the formation of tetrahydrofuran (THF) from 1,4-butanediol:

$$HO(CH_2)_4OH \rightarrow H_2O + (CH_2)_4O \quad (C)$$

and from HBB:

$$C_6H_5COO(CH_2)_4OH \rightarrow C_6H_5COOH + (CH_2)_4O \quad (D)$$

EXPERIMENTAL

Products

4-Hydroxybutyl benzoate and 1,4-butylene dibenzoate were synthesized as previously reported[1]. 3-butenyl benzoate (BB) was synthesized starting from benzoyl chloride and 3-buten-2-ol in a similar way. 1,4-Butanediol (BD) and titanium tetrabutylate $Ti(OBu)_4$ were commercial products; they were distilled at reduced pressure before use. Reagent grade benzoic acid (BA), zinc acetate, lithium acetate and potassium iodide, commercial potassium titanium oxalate and 'stabilizers' Irganox 1222, Irganox 259 and Irganox 1010 (produced by Ciba–Geigy) were dried before use.

Treatment of samples

All the different samples were introduced into glass tubes (6 mm inner diameter) weighted and sealed under reduced pressure of dry nitrogen.

In the temperature range between 210°C and 280°C tests were performed introducing the tubes in the holes of an aluminium block (15 cm long) which was electrically heated. The temperature was controlled within ± 0.5°C and the difference between the centre and the ends of the holes was about 1°C.

For tests performed in the range between 150°C and 190°C the tubes were placed in a thermostatically controlled oil bath, where the temperature was controlled within ± 0.1°C. After the appropriate time intervals, tubes were removed and quenched in an ice bath.

Analysis of reaction products

Benzoic acid was determined by titrations with an alcoholic solution of NaOH (0.02 N) with phenol red as an indicator. Measurements of the amount of tetrahydrofuran in the samples were carried out by g.c. with a Carlo Erba Fractovap mod. GV instrument. Carbowax 20 M 25% 30/60 Mesh columns were employed at 100°C; toluene was used as internal standard.

BDB and BB were evaluated among reaction products by an HPLC Perkin–Elmer instrument, equipped with a u.v. detector as previously reported[1].

Butadiene, collected in a gas cell, was identified by i.r. spectroscopy.

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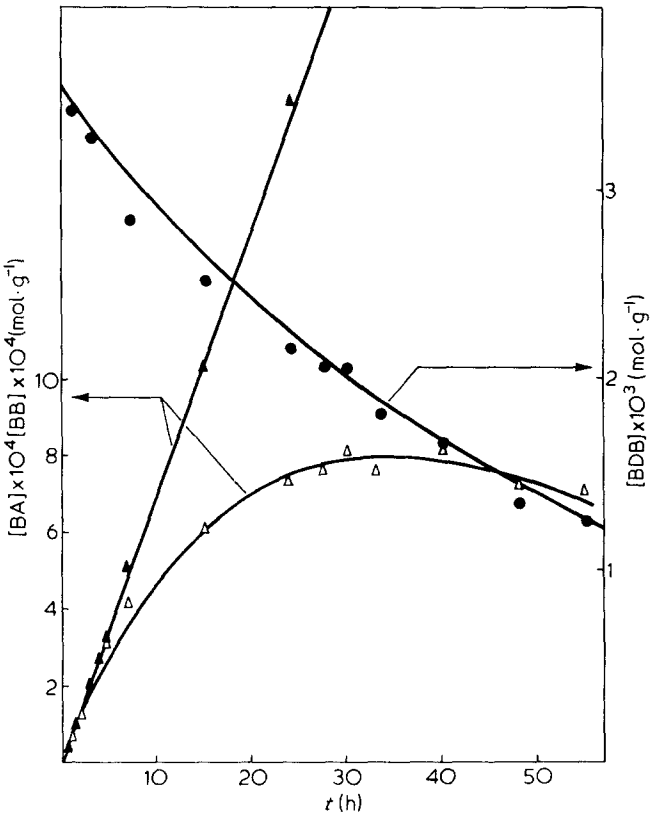


Figure 1 Theoretical (——) and experimental data for the thermal degradation of BDB at 280°C: (●), BDB; (△), BB; (▲), BA

RESULTS AND DISCUSSION

Reactions leading to degradation were studied in the temperature range between 210°C and 280°C.

Qualitative evidence for the formation of both 3-butenyl benzoate from reaction A and of butadiene from reaction B have been supplied respectively by *HPl.c.* and by i.r. absorption analysis of the volatile products. Since no other species were present, this result confirms the mechanism proposed elsewhere[2] for the polymer PBT.

At 280°C, for reaction A, first order kinetics with respect to BDB were found by experimental determinations of BDB concentration (data reported in *Figure 1*) up to an extent of reaction of about 60%. This result is in agreement with those reported for PBT and ethylene dibenzoate[3,4].

It is reasonable to assume that reaction B is also of the first order; accordingly, we can apply to reactions A and B together the usual treatment described[5] for series reactions.

The time at which maximum concentration of BB occurs is related to the kinetic constants by the equation

$$t_m = \frac{\ln \frac{k_A}{k_B}}{k_A - k_B} \qquad (1)$$

Moreover, the concentrations of the different substances involved are expressed by the following equations

$$[BDB] = [BDB]_0 e^{-k_A t} \qquad (2)$$

$$[BB] = [BDB]_0 \frac{k_A}{k_A - k_B} (e^{-k_B t} - e^{-k_A t}) \qquad (3)$$

$$[BA] = [BDB]_0 \left(2 + \frac{2k_B e^{-k_A t} - k_A (e^{-k_A t} + e^{-k_B t})}{k_A - k_B} \right) \qquad (4)$$

$[BDB]_0$ being the initial concentration of BDB, and $[BA]_0 = [BB]_0 = 0$. By means of equation (2) the value of the kinetic constant k_A has been calculated to be 52×10^{-7} s^{-1}. Since t_m is ranging between 35 and 40 h (see *Figure 1*) with the aid of equation (1) one finds for k_B a value between $1.6k_A$ and $2.2k_A$; equations (3) and (4) give the best results in accord with the experimental results for $k_B = 2.2k_A$. This is shown in *Figure 1*, where the calculated curves are also reported. Since two ester groups are present in the BDB molecule, and only one in the BB molecule, the reactivity of the ester groups in reaction B is about 4.4 times greater than in A.

The above results confirm that the determination of BA is a reliable method for measuring the extent of degradation, provided that reaction times are not too long (so that the effect of reaction B may be neglected) and temperature does not exceed 280°C (in order to avoid decarboxylation reactions[6,7]).

We carried out a first order kinetic treatment for reaction A alone: in these conditions, if $k_A t \ll 1$, $n_{BA}/n^0_{BDB} = 1 - e^{-k_A t} \simeq k_A t$ (n_{BA} and n^0_{BDB} being the number of mols of BA and the initial number of BDB mols respectively).

The results are shown in *Figure 2*: the increase of n_{BA} is linear, therefore a possible catalytic effect of BA being formed may be reasonably excluded. In *Table 1* the values of k_A are collected. These were found to be in accordance with those previously found for the corresponding reaction in the case of PBT[2,3]: although, in our earlier

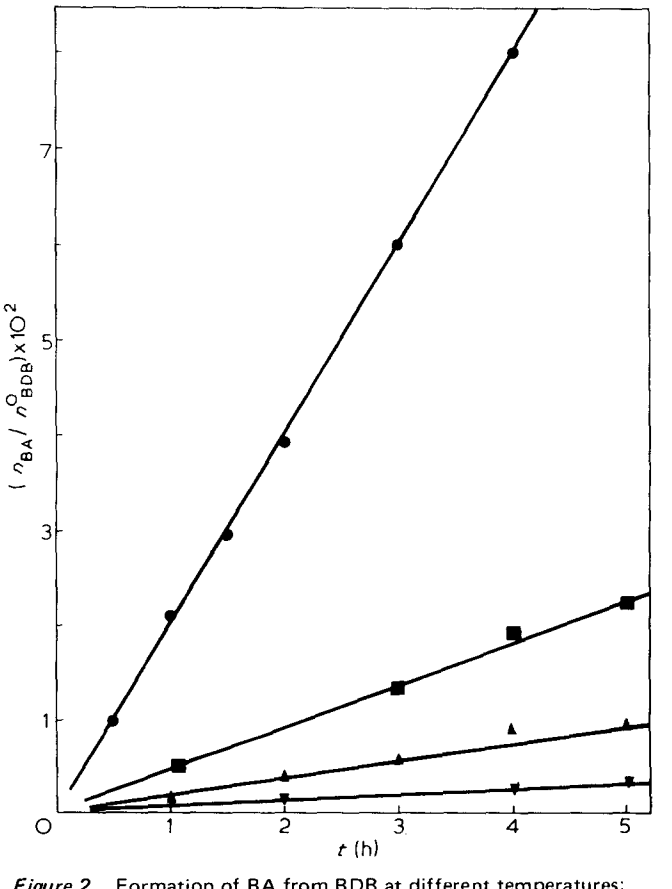


Figure 2 Formation of BA from BDB at different temperatures: (▼), T = 210°C; (▲), T = 250°C; (■), T = 260°C; (●), T = 280°C

Table 1 Kinetical parameters for reactions A, B and D

Reaction	T (°C)	$k \times 10^7$ (s^{-1})	E_a (kcal mol^{-1})
A	210	1.7	45.0
	250	5.0	
	260	13.0	
	280	52.0	
B	280	114.0	–
D	158	1.9	29.0
	167	3.6	
	180	9.4	
	190	19.2	

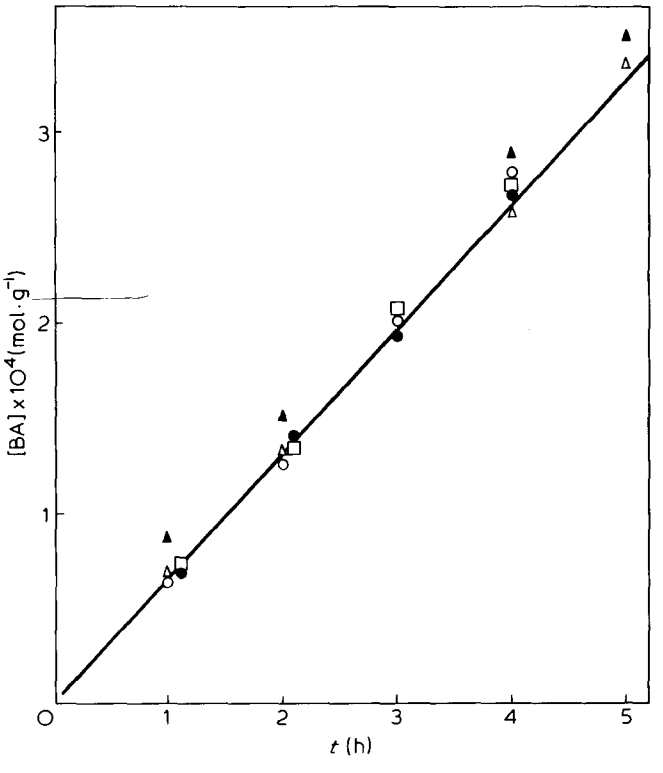


Figure 3 Formation of BA from BDB at 280°C. Without catalyst (——); with different catalysts added: (▲), $Ti(OBu)_4$, 6.63 x 10^{-7} mol g^{-1}; (△), $Ti(OBu)_4$, 6.63 x 10^{-6} mol g^{-1}; (●), TiK oxalate, 6.64 x 10^{-7} mol g^{-1}; (□), Li acetate, 6.63 x 10^{-7} mol g^{-1}; (○), Zn acetate, 6.63 x 10^{-7} mol g^{-1}

work[2] on PBT degradation, the splitting off of butadiene was found to be much faster than the first step, this is not strictly true in the present case. This is perhaps due to the absence of a carbonyl group in the *para* position.

The plot of ln k_A *versus* $1/T$ is linear in the range between 250°C and 280°C and leads to an activation energy of 45 ± 1 kcal mol^{-1}. The value of k_A found at 210°C is surprisingly high, perhaps by the effect of moisture traces, which show a relatively strong effect at this temperature.

The activation energy value is in good accordance with those previously found for PBT[2,3] and ethylene dibenzoate[8]. In view of this rather high value, the reaction of degradation is practically negligible, if compared with the 'useful' reactions, at temperatures below 210°C. It has been reported that catalysts can affect the degradation[9-11] in the case of poly(ethylene terephthalate), and that such reaction cannot be inhibited by the addition of 'stabilizers'[3,4]. A series of tests were carried out at 280°C on samples of BDB in which some of the catalysts used generally in polyester syntheses and of products claimed as improvers[12] or actually used as stabilizers were added in various amounts. The results appear in *Figures 3* and *4*. They show that neither catalysts nor 'stabilizers' have a significant effect on the initial rate of formation of benzoic acid, that is, on the merely thermal degradation: the small increase of BA in some cases can be ascribed to moisture traces in the additives. Furthermore, some tests were performed on BDB at 280°C for 40 h in the presence of various catalysts: BA and BDB concentrations were found to be unaffected by catalysts.

As to (ii) reactions, it is known that 1,4-butanediol can give rise to the formation of THF according to reaction C. It has been proposed[13,14] that the reaction takes place by an intramolecular etherification. To our knowledge the process has been kinetically studied[14] only in the presence of a large amount of hydrochloric acid, and in a range of temperatures quite different from ours. Therefore we studied reaction C both in the presence and in the absence of $Ti(OBu)_4$.

Our data are collected in *Figure 5* and seem to suggest an autocatalytic pattern, with a clear induction period. It is rather doubtful, however, that such an autocatalytic effect can be ascribed to water or to THF, since some tests carried out in the presence of calculated, large amounts of water (up to 33% by mols) and of small quantities of THF gave no significant increases in the production of THF. Reaction C likewise appears unaffected by the presence of

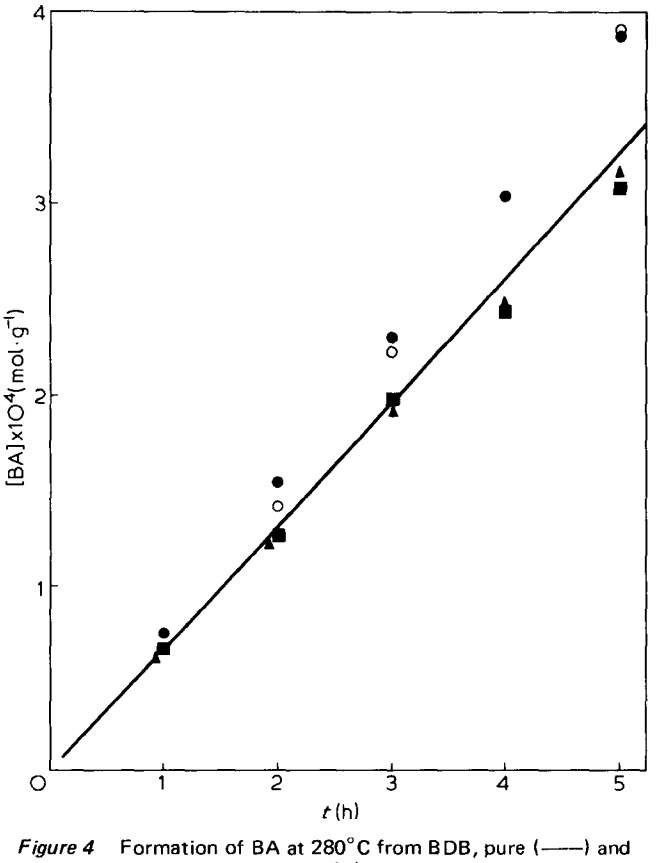


Figure 4 Formation of BA at 280°C from BDB, pure (——) and with different 'stabilizers' added: (●), Irganox 1222, 1.2% wt; (▲), Irganox 1010, 3.8% wt; (■), Irganox 259, 2.1% wt; (○), KI, 0.56% wt

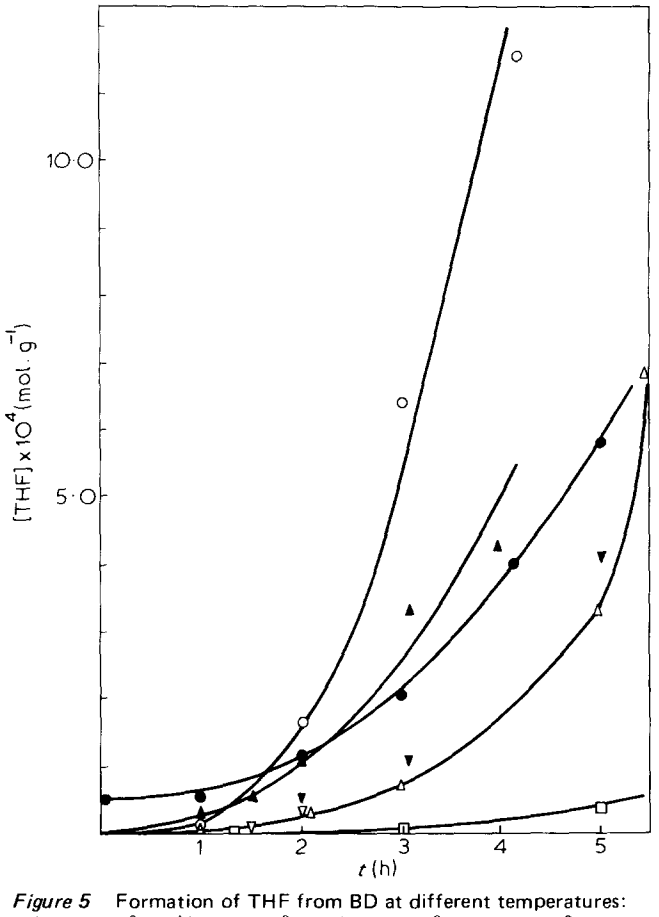


Figure 5 Formation of THF from BD at different temperatures: (□), T = 167°C; (△), T = 180°C; (○), T = 190°C; i.e. at 180°C with added: (▽), $Ti(OBu)_4$, 0.0068% mol; (●), THF, 0.48% mol; (▼), water, 33.4% mol; (▲), BA, 0.71% mol

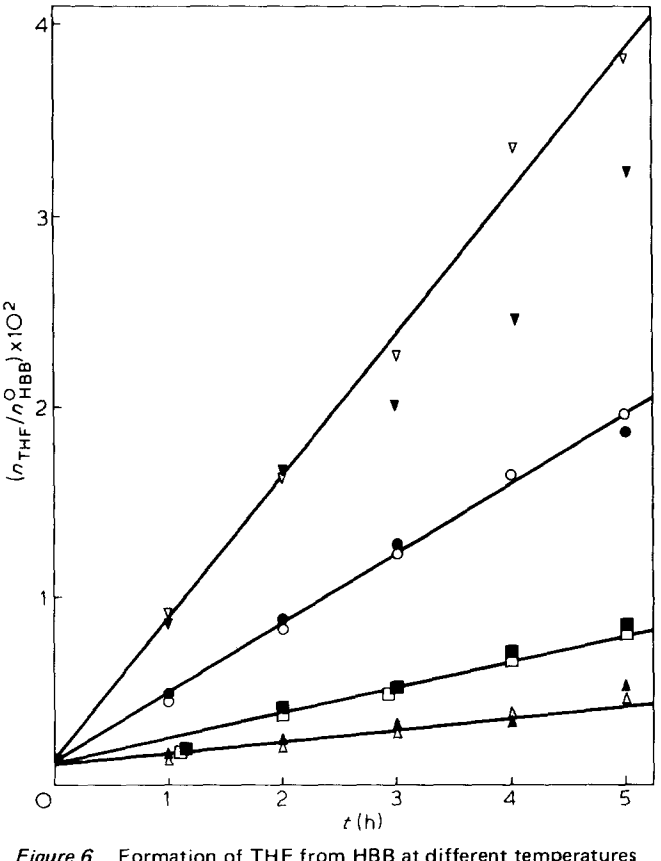


Figure 6 Formation of THF from HBB at different temperatures with $Ti(OBu)_4$, 6.70 x 10^{-7} mol g^{-1}, added: (▲), T = 158°C; (■), T = 167°C; (●), T = 180°C; (▼), T = 190°C. Without catalyst: (△), T = 158°C; (□), T = 167°C; (○), T = 180°C; (▽), T = 190°C

$Ti(OBu)_4$, instead, benzoic acid (0.7% by mols) exhibits a positive catalytic effect.

Reaction D was studied both in the presence and in the absence of $Ti(OBu)_4$. Experimental data of BA and THF formation are reported in *Figures 6* and *7*; the increases of n_{BA} and n_{THF} are linear, therefore a catalytic effect of BA may be reasonably excluded.

When catalyst is not added, the formation of BDB being practically avoided[1], the results are consistent with a first order kinetics with respect to HBB, and an activation energy of 29 kcal mol^{-1} (see *Table 1*) may be calculated, in accordance with that found elsewhere for THF formation from PBT[7].

In the presence of catalyst, THF can of course derive both from HBB and from 1,4-butanediol arising in the faster 'polycondensation' process:

$$2C_6H_5COO(CH_2)_4OH \rightleftarrows C_6H_5COO(CH_2)_4OCOC_6H_5 + HO(CH_2)_4OH$$

Our data show that the catalyst has no significant effect on the formation of tetrahydrofuran. However, it is not possible in this case to account for the experimental results by a global kinetic treatment, owing to the presence of benzoic acid which is formed in the reaction and has an incompletely understood inhibiting effect on the polycondensation[1] and accelerates the formation of THF from BD. The formation of THF from breaking of in-chain ester linkages, involving an ionic mechanism via unsaturated end groups as reported for PBT[7], has not been found by these authors. Indeed THF has not been recognized among the volatile products arising from BDB (when BB is present). In view of the value of the activation

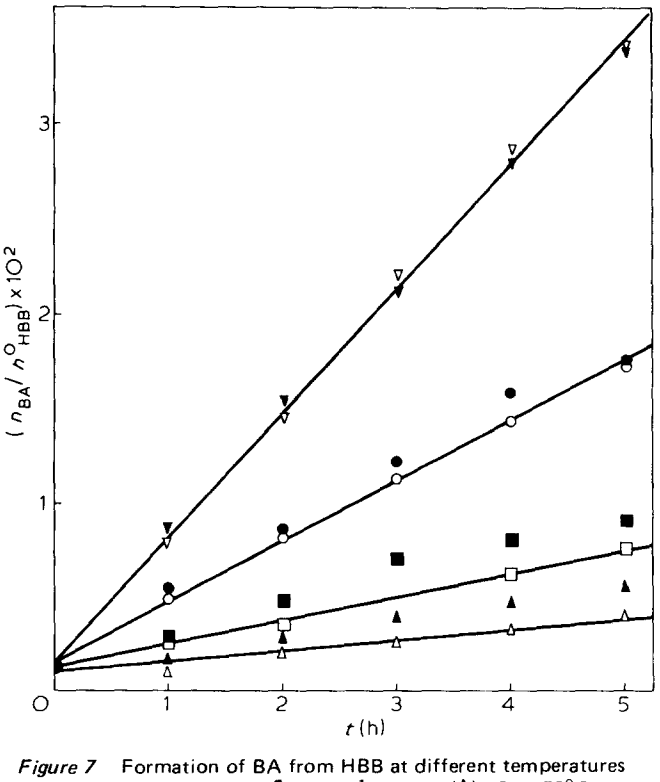
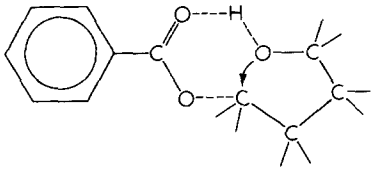


Figure 7 Formation of BA from HBB at different temperatures with $Ti(OBu)_4$, 6.70 x 10^{-7} mol g^{-1}, added: (▲), T = 158°C; (■), T = 167°C; (●), T = 180°C; (▼), T = 190°C. Without catalyst: (△), T = 158°C; (□), T = 167°C; (○), T = 180°C; (▽), T = 190°C

energy of reaction D (29 kcal mol^{-1}) in accordance with that found for the formation of THF from PBT (27.9 kcal mol^{-1}), it may be proposed that in PBT also, the formation of THF takes place through an intramolecular mechanism via a cyclic intermediate of the type:



It may be recalled that for the formation of THF from 1,4-butanediol an analogous mechanism has been proposed[14] with an activation energy of 30.9 kcal mol^{-1}.

CONCLUSIONS

Our experimental data, as well as those reported by other authors[3,6,7] lead us to conclude that the secondary reactions of some importance in the PBT polymerization are the following: in a relatively low temperature range (160°–210°C) only the reactions giving rise to THF are to be considered. Between 210°C and 280°C the reactions involving the breaking of ester linkages[2,3,6,7] also become important. All these reactions are not significantly affected by the presence of $Ti(OBu)_4$. At temperatures above 280°C decarboxylation reactions cannot be neglected, and their importance increases strongly above 300°C.

To measure the extent of polyester degradation, the determination of the number of COOH end groups is widely used. This method, although it has been recently criticized for poly(ethylene terephthalate)[4] appears nevertheless reliable, from our data, for PBT, provided that it is applied to the extent of low degradation and that the contemporary formation of COOH from OH end groups (reaction D) is taken into account. Moreover, our results confirm that the breaking of an in-chain ester linkage takes place via an intramolecular cyclic intermediate, as has been often described for various kinds of esters. Such an intermediate takes place when hydrogen atoms are available in β position with respect to the ester linkage; it seems impossible to prevent this reaction with the aid of additives; likewise, it may be supposed that this is also true for reaction D.

In the case of PBT and of its model BDB the formation of butadiene occurs as a consequence of primary and secondary breaking of the ester linkages. The secondary breaking is a faster reaction than the primary one; however, a number of unsaturated end groups will be present in the polymer bulk. In the case of actual PBT polymerization, in view of the E_a values of reactions A and D and of the effect of catalysts added, one can predict that it will be useful to operate at temperatures as low as possible and in the presence of rather high catalyst concentrations. During the polycondensation the COOH end groups arising in the secondary reactions will react with hydroxyl groups as long as these will be available: an upper limiting value of molecular weight will result, together with a loss of 1,4-butanediol, stoichiometrically transformed into THF.

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